



Reactive and Nonreactive Binders in Glass/Vinyl Ester Composites

by John C. Brody and John W. Gillespie, Jr.

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September 2004

prepared by

**University of Delaware
Center for Composite Materials
Newark, DE 19716**

under contract

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14. ABSTRACT This study characterizes and evaluates two types of preform binders—reactive thermosets and nonreactive thermoplastics. The interply adhesion between woven glass plies was measured as a function of binder type, concentration, and preforming conditions. It was found that reactive binders offer the potential to provide much larger interply adhesions between glass plies in a preform than thermoplastics and are thus superior choices for the fabrication of complex-shaped preforms requiring little or no springback. Laminated composite panels fabricated from preforms with varying binder concentrations were evaluated in regards to their interlaminar properties. It was found that both binder types degraded the interlaminar shear strength of a woven glass reinforced/vinyl ester composite. Additionally, composite laminates made from preforms and containing the thermoplastic binder showed decreases in the interlaminar fracture toughness of the composite by ~60%. However, composite laminates fabricated from preforms using the reactive epoxy binder showed an increase in fracture toughness by ~47%. Hence, it is concluded that a range of interlaminar properties can be achieved depending on the type of binder, the amount of binder, and the processing of the binder, and also that of the composite itself.				
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1. Introduction

Liquid composite molding processes such as vacuum-assisted resin transfer molding (VARTM), resin transfer molding (RTM), and the Seeman composite resin infusion molding process (SCRIMP) have been recognized as low-cost methods in manufacturing large-size composites in the marine, transportation, and civil infrastructure industries. Such manufacturing processes usually require the reinforcement material, typically two-dimensional (2-D) fabrics layers, to be hand laid into a mold cavity prior to processing. This often requires multiple layers of reinforcement mat to be cut to shape, stacked, and aligned to conform to various curvatures of the mold cavity (1). In order to reduce production time and cost, preshaped reinforcement, or preforms are often employed. Preforms typically consist of multiple layers of dry reinforcement mat, bound together into a single, three-dimensional (3-D), net-shaped structure.

Additional benefits of using preforms include easy handling and mold placement of the reinforcement material, control of fiber alignment, prevention of unwanted wrinkling of layers, the ability to control part thickness to meet dimensional tolerances, and the ability to control the fiber volume fractions that will be present in the final cured composite itself.

Preforms can be fabricated by complex weaving processes and/or stitching of individual reinforcement plies. Preforms may also consist of layers of reinforcement mats, which have been bound together by polymeric materials, most often referred to as binders or tackifiers. The most common types of binders are typically low-melting thermoplastic polyester, or either catalyzed, or uncatalyzed thermosetting epoxies that are solid at room temperature (2–4). Thermoplastic and uncatalyzed binders are typically designed to be soluble in the infusing matrix, whereas reactive (catalyzed) binders are often designed to react and be compatible with the matrix resin.

Binders can be applied to the reinforcement fabric surface in various methods. Common application methods use veils, solvent spray, and powder. Veils are placed between adjacent plies of reinforcement material, and ply stacks are fused together into a preform upon application of heat and pressure (2). In the case of spray application, the solid binder is dissolved into a solvent, commonly acetone, and applied by a spray gun to the fabric surface. Some researchers have found that this method of application provides for a more uniform coverage of the binder material (5); however, this is often times not feasible due to inherent health hazards and additional requirement for solvent removal.

Another commonly used tackifier application approach is to use powders. Powdered preform binders are required to be distributed uniformly onto the surface of the fiber mat in order to ensure sufficient adhesion throughout the preform. Typical binder loadings range from 4% to 7% of the weight of the reinforcement (2, 4, 6). After the binder is applied to the fiber mat

surface, sufficient heat is next applied to the mat in order to melt the binder material. This is usually done with the use of infrared lamps or ovens. Then upon cooling, the binder resolidifies, adhering to the fiber mat surface.

Preforms are then constructed from individual plies of binder-coated mats by any typical thermoforming process involving heat and pressure. The individual plies are stacked, aligned, and placed within a mold cavity. Pressure is typically applied by a mechanical press, or by a vacuum bag assembly. Again, adequate heat is applied to melt the binder, and react the binder in the case of reactive thermosetting binders. Heat is often applied via a heated tool or the mold being placed in an oven or autoclave. Once the binder is allowed to melt on the surface of the fiber mats, the assembly is allowed to cool while a constant pressure is maintained. Upon cooling, the binder resolidifies, and the individual plies are fused into a single, net-shaped preform.

The use of preform binders introduces significant issues requiring attention, including springback, shape retention, permeability and wet-out of the preform; binder dissolution and migration; and affects on the matrix resin and overall performance of the composite.

A few studies have addressed the effect of preform processing and binder type on the shape retention of preforms. Studies conclude that preform springback is dependent upon the binder modulus, ply surface area coverage, extent of binder reaction, and binder location (interply vs. intraply). Accordingly, higher binder modulus, surface coverage areas, and reactivity conversion all result in less springback (2, 4, 7). Additionally, the binder location has shown to affect both springback and interply adhesion. Studies have shown that both type of binder application (spray vs. powder) and performing conditions can influence whether the binder will penetrate within fiber tows or remain on the layer surface (2, 7, 8). Results from these studies indicate that preforms with binder inside fiber tows offer far less springback, whereas those with binder that remains outside fiber tows and solely on fiber mat surface offer superior interply adhesion.

Another significant issue is the effect binder materials impart on the permeability and fiber wet-out. Studies indicate that permeability is affected more by the blockage of the larger gaps between the fiber tows (interlayer) as compared to the blockage of the smaller interstitial gaps within the tows (intralayer) (4, 7, 9). For preforms in which the tackifier remains outside the fiber tows, the permeability decreased as the tackifier concentration increased (4, 7). In contrast, for fabrics preformed at higher temperatures, in which the binder infiltrates within the fiber tows, the preform permeability increased as the binder concentration increased (7). However, in the case where binder is predominantly within the fiber tow, results indicate poor wet-out, and formation of voids within the tows (4).

Additionally, it has been shown that binder dissolution can cause drastic increases in resin viscosity, and thus hinder mold filling as well (3, 9). Furthermore, uneven dissolution and binder migration can result in varying binder concentrations across the cured composite laminate (2, 3),

which may result in uneven shrinkage and a distribution of reaction rates, mechanical properties, and thermal stresses within the composite part.

Additional studies have shown that preform binders can have a drastic effect on the thermophysical and mechanical properties of the matrix resin and overall composite laminate. Studies have shown binder material may alter resin fracture toughness, tensile strength and strain, impact energy, and glass transition temperatures (2, 9–11).

Additionally, the use of incompatible binders has been shown to have detrimental effects on a composite laminates interlaminar strength and toughness. It has been suggested to choose a compatible binder with similar chemistry to that of the parent resin matrix for best composite performance (2). Moreover, it has been shown that modifying binders with elastomer particles can provide for significant increases in interlaminar toughness (5, 6).

In the present study, two types of preform binders are investigated: a reactive epoxy, and a nonreactive thermoplastic polyester. The interply adhesion between woven glass plies was measured as a function of binder type, concentration, and preforming conditions. Additionally, the effects of the respective binders on the interlaminar properties of a vinyl ester composite were addressed.

2. Experimental

2.1 Materials

In this study, two different types of preform binders were evaluated. ATLAC^{*} 363E, a thermoplastic polyester, and PRETEX 110, a catalyzed epoxy with a heat activated curing agent. The reinforcement used in this study was E-glass Vetrotex 324 0°/90° woven roving with an aerial weight of 24 oz/yd². The sizing of the E-glass was Vetrotex product #611, which consisted of a vinyl ester/polyester-compatible silane coupling agent and an epoxy film former. The resin of interest was a vinyl ester, Dow DERA KANE[†] 411-C-50, containing 50% styrene monomer by weight.

As seen from its respective dynamic scanning calorimetry (DSC) profile (figure 1), the ATLAC binder has a melting temperature at ~55 °C and a glass transition temperature of 47 °C. The reactive nature of the PRETEX binder is evident in its DSC profile (figure 2). From figure 2, it is seen that PRETEX has a melting temperature at ~60 °C, and upon further heating it is observed that an exothermic reaction is taking place, beginning at ~75 °C, and peaking at ~115 °C. The resulting cross-linked polymer was found to have a glass-transition temperature at ~110 °C.

^{*} ATLAC is a registered trademark of Reichhold Chemicals.

[†] DERA KANE is a registered trademark of the Dow Chemical Company.

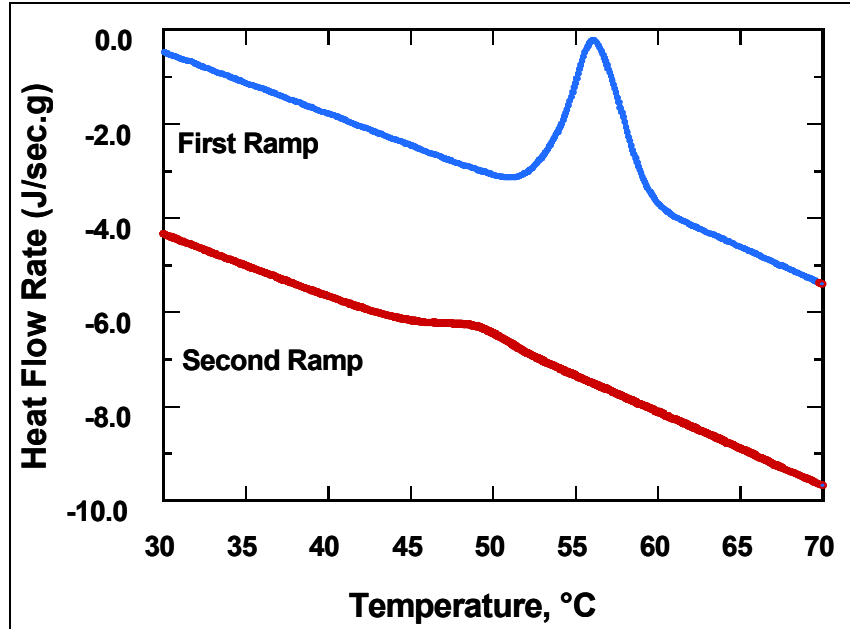


Figure 1. DSC thermogram of ATLAC 363E showing glass-transition temperature and melting temperature.

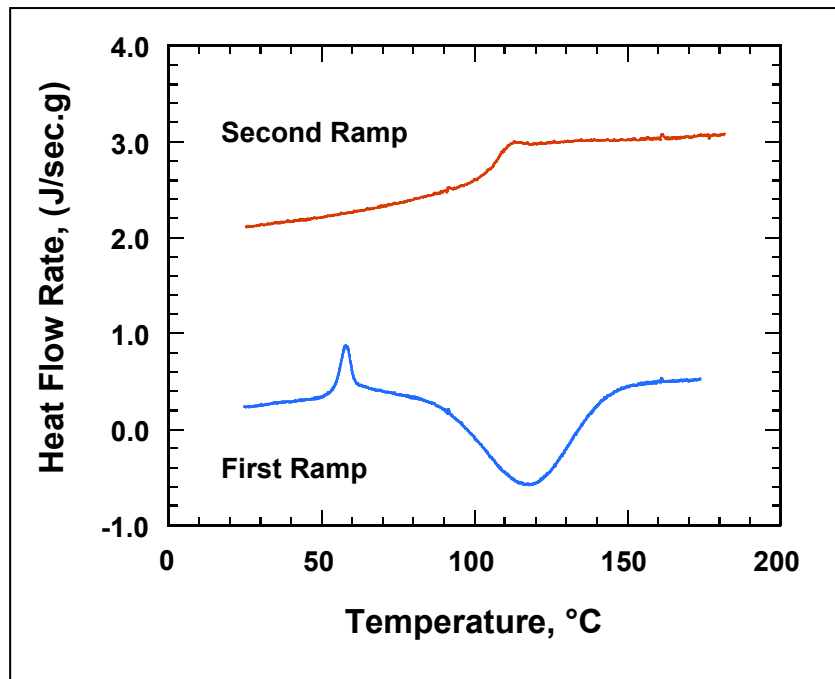


Figure 2. DSC thermogram of PRETEX 110 showing glass-transition temperature and melting temperature.

2.2 Preform Construction

Preforms consisting of varying binder concentrations of 3, 6, and 9 weight-percent for both binders were constructed, where the weight percentage is based on that of the dry reinforcement

only. The powdered binder particles were first applied uniformly to the surface of individual fiber plies via a handheld sifter-type apparatus. Subsequently, the mats were placed in a noncirculating oven at 65 °C for ~10 min in order to adhere the binder particles to the mat surface. Next, individual binder-coated plies were stacked and aligned on one another and placed on a flat tool surface within a vacuum bag assembly. The assembly was then placed back in the oven and vacuum and heat were applied to fuse the plies into a flat-shaped preform. The heat allowed the binder to melt (and react in case of PRETEX), and the pressure served to consolidate the preform. Subsequently, the bag assembly was removed from the oven while vacuum pressure was maintained in order to maintain compaction until the binder cooled and resolidified. Preforms with the ATLAC binder were processed at a temperature of 80 °C for 30 min, whereas those with the PRETEX binder were processed at 110 °C for 2 hr to ensure complete cross linking of the binder during preforming.

2.3 Composite Fabrication

Composite laminates were manufactured from the preforms using a VARTM technique. Preforms consisted of 8 plies of reinforcement at dimensions of 40 × 40 cm (15 × 15 in), with varying concentrations of 3, 6, and 9 weight-percent, or each respective binder. The preforms were placed on a flat mold surface within a vacuum bag assembly and infused with the vinyl ester resin at room temperature. Following complete infusion and cure of the resin, the composite laminates were demolded and postcured in an oven at 130 °C for 2 hr.

2.4 Preform Characterization

Preforms were analyzed for binder coverage, spread out, and tow impregnation at their respective processing specifications by a scanning electron microscope (SEM). Additionally, their interply adhesion was evaluated by a T-peel test in accordance to ASTM D 1876 (12). This test method determines the relative peel resistance of adhesive bonds between flexible adherands, where the material peel strength is measured as the force per unit width required to pull apart the two adherends. Preforms (12 × 12 in) were constructed, consisting of two layers of woven glass mat bound with binder material at varying concentrations of 3, 6, and 9 weight-percent. Specimens were sectioned from these preforms at dimensions of 7.6 × 30 cm (3 × 12 in). Specimens manufactured with the ATLAC binder were preformed at a temperature of 80 °C for ~30 min. Two sets of specimens were manufactured with the PRETEX binder. The first set was processed at 110 °C for 2 hr and the second set at 65 °C for 30 min. Based on the binders melting and reaction temperatures of 65 and 110 °C, as determined from DSC, it is expected that the binder is fully reacted and cross linked in the first set of specimens, and little or no cross linking is achieved in the second set of specimens. The specimens were tested on an Instron tensile testing machine with a constant crosshead displacement of 25.4 cm (10 in)/min at ambient conditions.

2.5 Composite Performance

Following the fabrication of the composite laminates, their respective fiber volume and void contents were determined. Void content was calculated by determining the actual measured density of a composite and comparing it to a theoretical density. The volume of voids was computed from the following equation:

$$V = (T_d - M_d) / T_d, \quad (1)$$

where V is the volume percent of voids within the composite and M_d and T_d are the measured and theoretical densities of the composite laminate. The measured density of the material was determined by the dry/wet weight method outlined in ASTM D 792 (13). The theoretical density was calculated based on the individual mass fractions of the constituents, in which the fiber mass fraction was determined by a burnout test, and the binder mass fraction was based on the original binder loading onto the glass mats during preforming.

The apparent interlaminar shear strength of the composite specimens was determined in accordance to ASTM D 2344 (14), using a short beam shear test. The eight layers of glass ply resulted in a composite laminate with an approximate thickness of 0.5 cm (0.20 in). In order to ensure specimens fail in shear, it is recommended by the standard to use a length to thickness ratio of 7, for glass fiber reinforced composites. Thus, specimens were cut from the flat composite laminates at a length of 3.5 cm (1.4 in) and a width of 1.5 cm (0.6 in). A span-to-thickness ratio of 5 is suggested, thus a testing span of 2.5 cm (1.0 in) was used. Specimens were loaded in an Instron tensile testing machine fixture in three-point bending at a span of 2.5 cm (1.0 in) and a testing speed of 0.13 cm (0.05 in)/min. The apparent interlaminar shear strengths (S_H) were calculated as follows:

$$S_H = \frac{0.75P_B}{bd}, \quad (2)$$

where, P_B equals the failure load and b and d equal the width and thickness of the specimen, respectively.

The Mode I interlaminar fracture toughness of the specimens was determined in accordance with ASTM D 5528 (15). Dual cantilever beam (DCB) specimens were machined from the prefabricated composite panels at dimensions of 25.4 cm (10 in) in length and 2.54 cm (1.0 in) in width. Kapton* film was used as the nonadhesive insert and provided an initial crack length of ~6.4 cm (2.5 in). Opening forces were applied to the DCB specimen by means of loading blocks that were bonded with an epoxy adhesive to one end of the specimen. The DCB specimens were tested at ambient conditions with a screw-driven Instron tensile testing machine at a constant crosshead speed of 0.254 cm (0.10 in)/min. The opening crosshead displacement and load were recorded by the testing machine, whereas the propagating crack length was recorded by hand

* Kapton is a registered trademark of DuPont.

with the aid of a traveling magnifying glass. The Mode I critical strain energy release rate, G_{IC} , was calculated use modified beam theory by

$$G_{IC} = \frac{3P\delta}{2b(a + |\Delta|)}, \quad (3)$$

where P is the applied load, δ is the load point displacement, b is the width of the specimen, a is the crack length, and Δ is a correction factor determined experimentally and is equal to the difference between the x intercept and $x = 0$ points on the least-square plot of cube root of the compliance (y-axis) as a function of delamination length (x-axis).

3. Results and Discussion

3.1 Preform Analysis

Figures 3 and 4 show the surface of the fiberglass mat with varying binder loadings of 3 and 9 weight-percent of ATLAC and PRETEX binders. As the binder loading is increased, the surface area coverage increases. It is seen that the two types of binders exhibit similar binder coverage and spread out, and the binder materials remain on top of the fiber mat surface. Figure 5 displays the side view of the binder coated mats, where it is clearly seen that binder spread out is limited at these respective processing temperatures (80 °C for ATLAC and 110 °C for PRETEX), and the binder does not impregnate into the fiber tows. Additionally, it was found that preforms constructed with the PRETEX binder were much more stiff and “board-like” than those fabricated with the ATLAC binder.

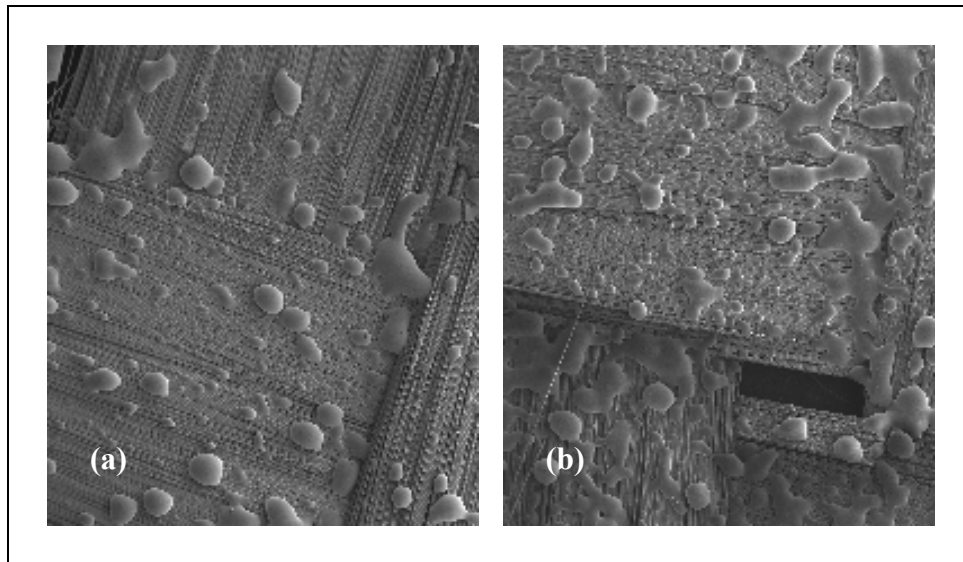


Figure 3. SEM image showing binder coverage of 3 weight-percent (a) and 9 weight-percent (b) ATLAC binder on woven glass mat processed at 80 °C.

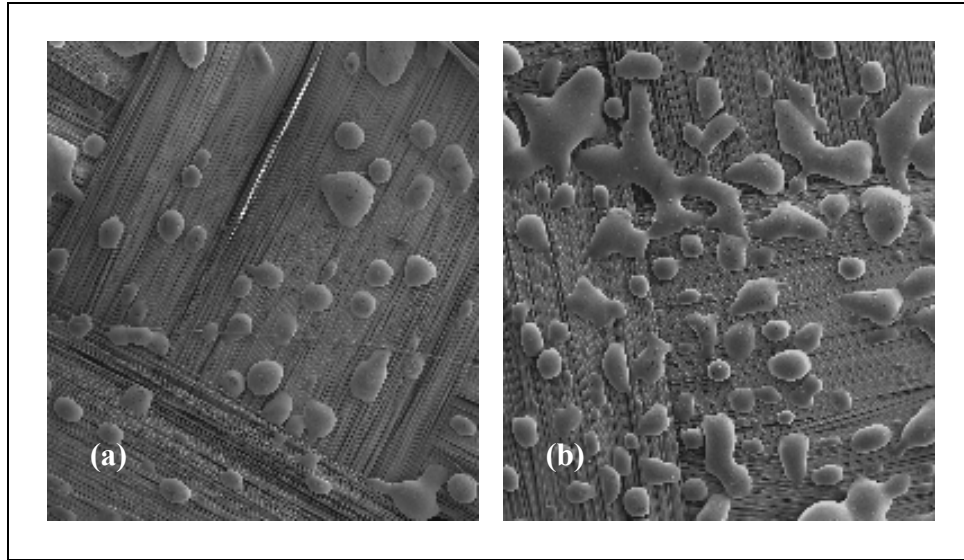


Figure 4. SEM image showing binder coverage of 3 weight-percent (a) and 9 weight-percent (b) PRETEX binder on woven glass mat processed at 110 °C.

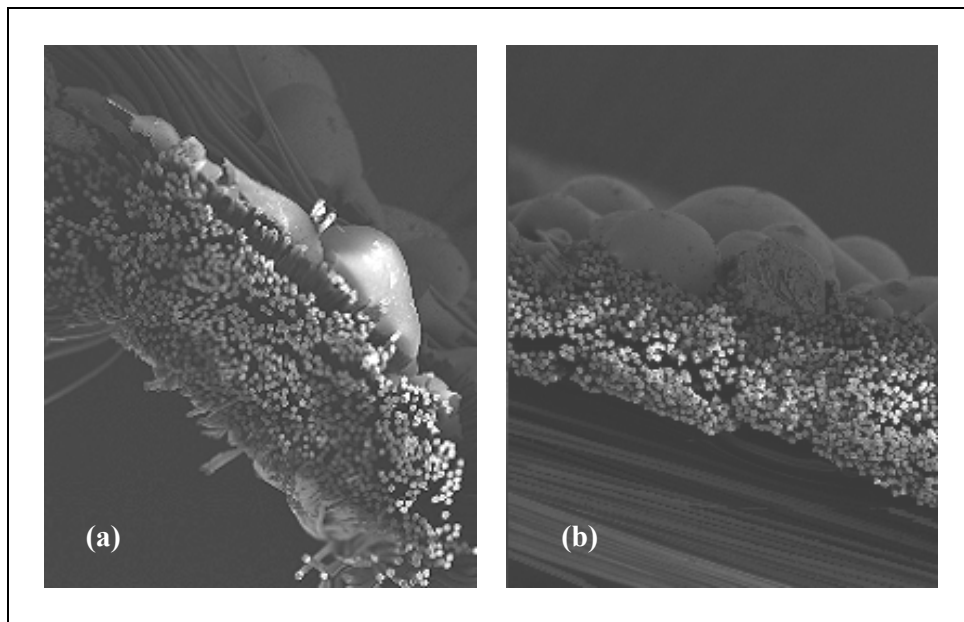


Figure 5. SEM micrographs showing the limited tow impregnation (a) of ATLAC binder processed at 80 °C and (b) PRETEX binder processed at 110 °C.

3.2 Interply Adhesion of Preforms (T-Peel Test)

The interply adhesion of the preforms was evaluated with a T-Peel test. Results of the test can be found in table 1 and figures 6 and 7. Typical load-vs.-displacement curve for the T-Peel test can be observed in figure 6. It was observed that the specimens exhibited a stick/slip type behavior, which is due to the uneven distribution of binder on the fiber mat surface and also

Table 1. Results of T-Peel test for 0°/90° woven E-glass tackified with ATLAC 363E and PRETEX 110 binders.

Binder Type	Peel Strength, (N/cm)		
	3 Weight-Percent	6 Weight-Percent	9 Weight-Percent
PRETEX 110 reacted	7.85 ± 2.61	15.52 ± 3.87	24.50 ± 2.96
PRETEX 110 unreacted	0.103 ± 0.028	0.166 ± 0.051	0.166 ± 0.026
ATLAC 363E	0.653 ± 0.186	1.21 ± 0.354	1.64 ± 0.527

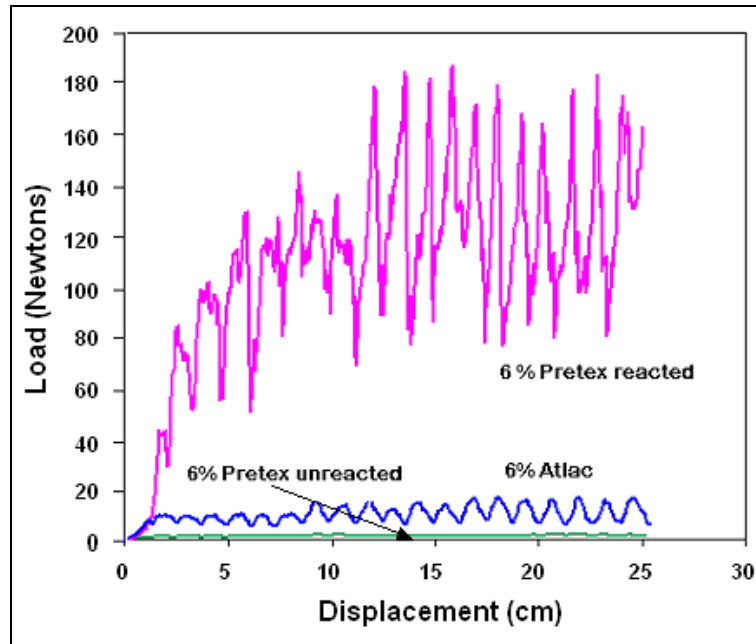


Figure 6. Load-vs.-displacement curve for T-Peel test of 3-in-wide specimen of E-glass with 6 weight-percent of varying binder type.

perhaps to the wavy architecture of the woven mat. Both factors would contribute to areas where the two plies do not perfectly adhere together. This stick/slip behavior became more pronounced at higher binder concentrations for each respective sample set.

The results from the peel test show that interply adhesive strengths increase as the binder loading is increased. This can be attributed to higher surface area coverage of the binder material. Results from the T-Peel test show that there is a much greater interply adhesion (15× greater at 9 weight-percent binder loading) for preforms constructed with the reactive epoxy (PRETEX) binder than those with a low-melting thermoplastic (ATLAC). It is believed that the thermoplastic binder simply provides a mechanical interlocking between adjacent plies, whereas if processed correctly, the reactive epoxy binder can provide an additional chemical adhesion with the fiber sizing. This, in turn, will result in much better interply adhesion, resulting in a more board-like preform with greater structural integrity. It was also found that specimens in

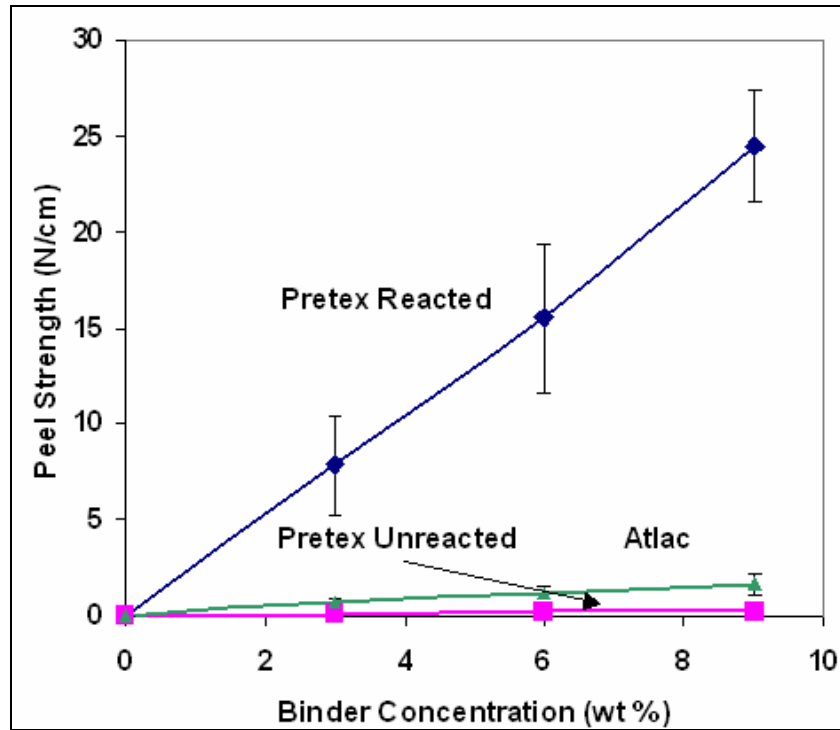


Figure 7. Peel strength vs. binder concentration for ATLAC and PRETEX binders on woven E-glass mats.

which the PRETEX binder was not reacted (processed at 65 °C for 30 min) exhibited very low adhesion. At this lower processing temperature, the binder material softens but is not allowed to flow and spread across the mat surface, or to undergo any crosslinking. Additionally, it was found that much of the binder could be easily brushed off the fiber mat surface due to poor adhesion. Thus, it is concluded that processing temperatures of 65 °C and lower are not adequate for preforms using PRETEX as the binder material.

The difference in interply adhesion between the reacted PRETEX and ATLAC specimens is also portrayed in the respective specimens failure. Samples made with the ATLAC binder exhibited a clean separation, whereas those made with the reacted PRETEX binder did not. From figure 8 it can be seen that the PRETREX specimens exhibited a “spider-webbing” type failure, resulting from the high adhesion that causes fiber bridging between plies. This bridging of fibers is also evident in the SEM image shown in figure 9. The SEM image in figure 10 also reveals that the predominant type of failure in both sets of specimens was an adhesive failure between the fiber and the binder material. Additionally, it appeared that ATLAC is a more brittle binder with the existence of fracture and cracking through the binder material.

3.3 Void Content Determination

Following the fabrication of the composite laminates, their respective fiber volume and void contents were determined. These factors are significant in that often times they influence the

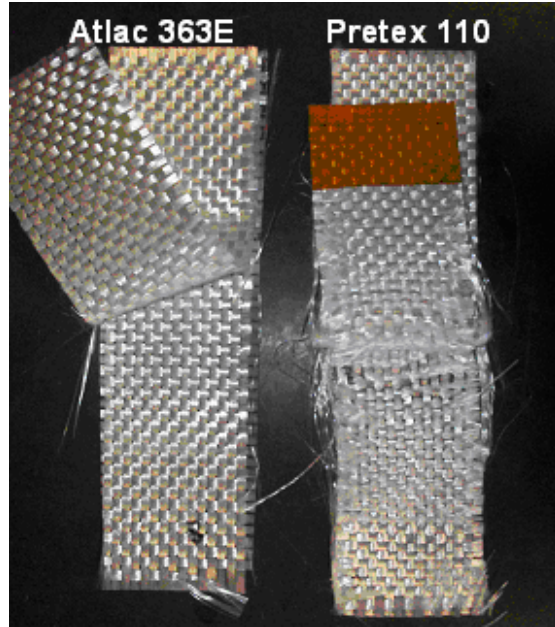


Figure 8. Comparison of T-Peel test specimens bound by ATLAC and reacted PRETEX binder on 0°/90° woven E-glass.

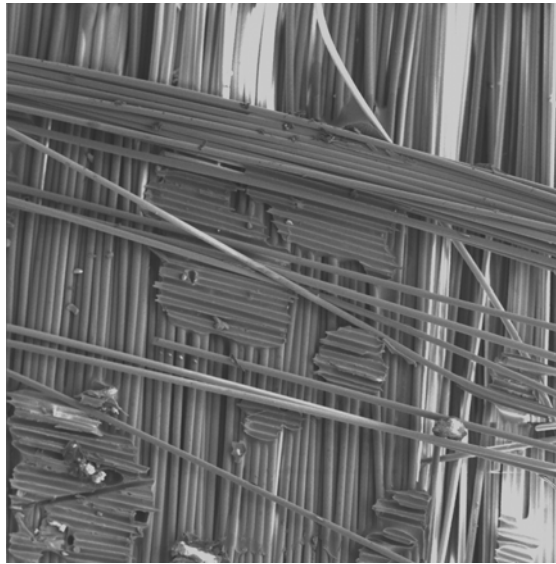


Figure 9. SEM micrograph of fiber mat surface of 6 weight-percent reacted PRETEX peel specimen at magnification of 75×.

mechanical response of the composite laminate. The results of the void and fiber contents of the composites are summarized in table 2.

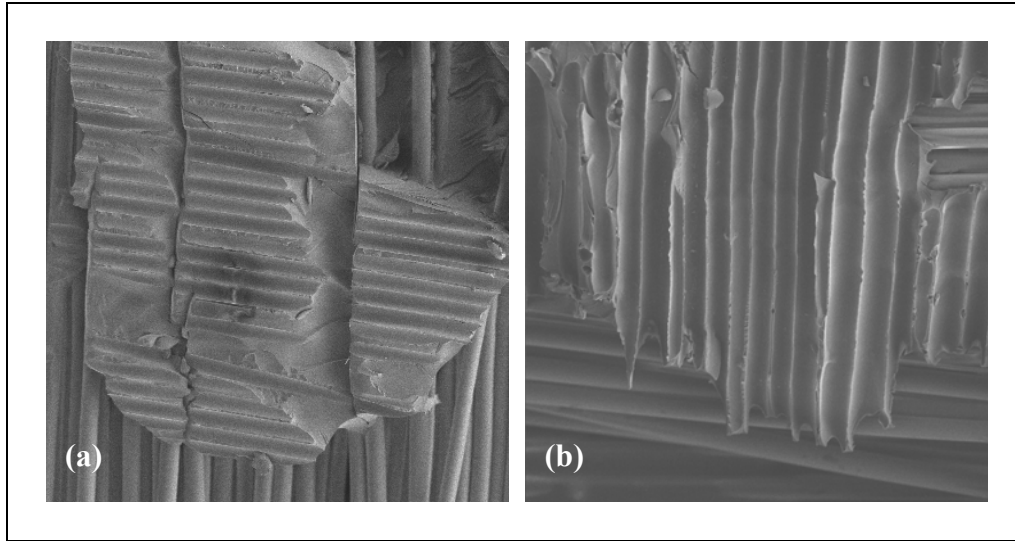


Figure 10. SEM micrographs of fiber mat surface of (a) 6 weight-percent ATLAC peel specimen at 200 \times and (b) 6 weight-percent reacted PRETEX peel specimen at 250 \times .

Table 2. Fiber volume fraction and void content of glass-reinforced vinyl ester composite laminates with varying binder concentrations.

Binder Loading	ATLAC 363E		PRETEX 110	
	V_f %	V_v %	V_f %	V_v %
No binder	47.5 \pm 0.5	1.78 \pm 0.21	47.5 \pm 0.5	1.78 \pm 0.21
3%	48.0 \pm 0.6	1.63 \pm 0.28	49.4 \pm 2.4	2.11 \pm 0.24
6%	47.9 \pm 0.9	1.99 \pm 0.57	53.7 \pm 1.6	4.64 \pm 1.71
9%	51.2 \pm 1.9	3.00 \pm 1.76	55.6 \pm 0.4	3.26 \pm 1.03

The fiber volume fractions of the composite laminates are ~48%–50% with the exception of the two laminates containing 6% and 9% PRETEX binder, which are slightly higher. From table 2, it is also seen that the composite laminates containing 6 and 9 weight-percent PRETEX binder had the highest void contents, although the standard deviations are moderately high. This greater fiber volume fraction may be attributed to less preform springback during infusion with the PRETEX preforms than the ATLAC preforms, due to the high interply adhesion as previously mentioned. Additionally, the ATLAC binder was soluble in the infusing resin, whereas once cross linked, the PRETEX binder is not.

SEM was also done to examine the void contents of the samples. The results from this analysis can be seen in figures 11 and 12. From the SEM micrographs, it can be seen that all of the composite samples contained some voids. It can be seen that the voids in the composite laminate without binder are relatively small in comparison to the larger voids in the laminates with binder material. As noted in the figures, the composites with 9 weight-percent PRETEX and

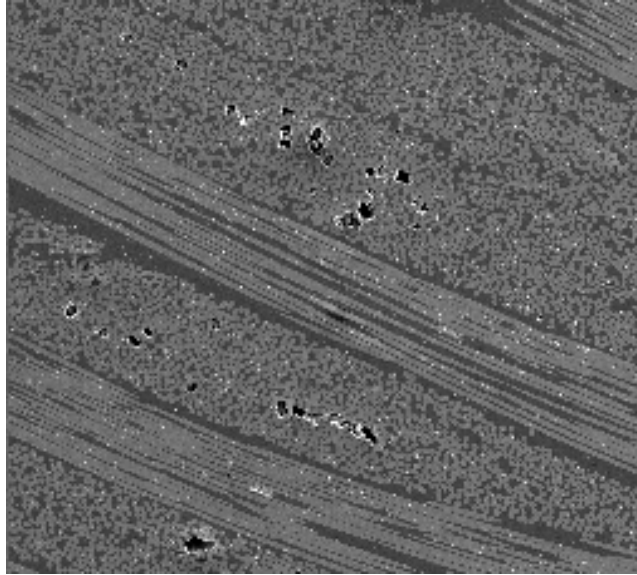


Figure 11. SEM micrograph of woven glass fiber vinyl ester DERAkANE 411-C-50 composite laminate with no binder at 55 \times magnification.

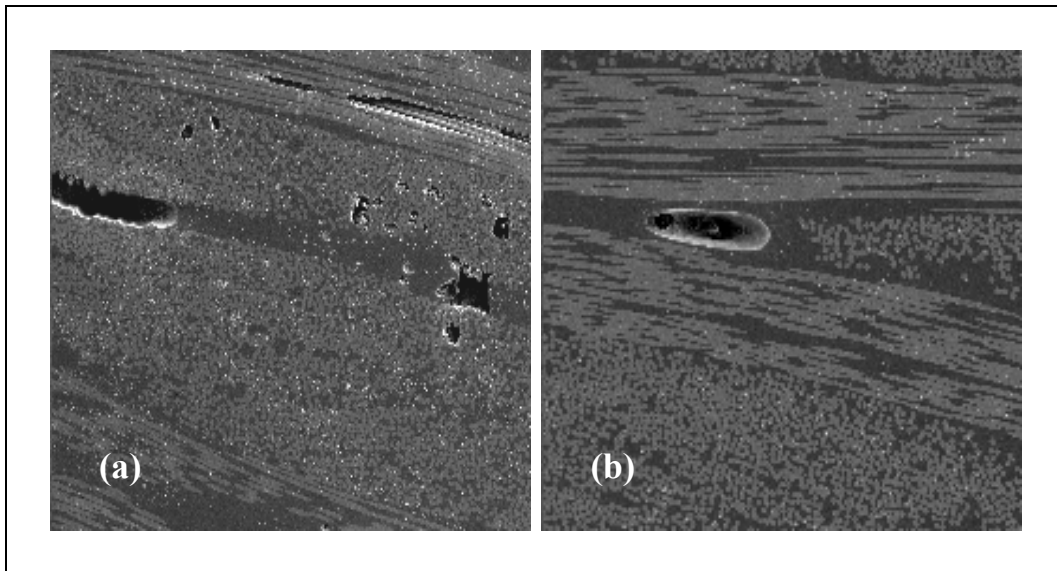


Figure 12. SEM micrograph of interlaminar void within composite laminates with (a) 9 weight-percent PRETEX binder and (b) 9 weight-percent ATLAC at 60 \times .

9 weight-percent ATLAC had large voids concentrated in the interlaminar regions and small voids within the fiber tows. The composite without binder also contained small voids within the fiber tows, but contained minimal interlaminar voids. This suggests that the binder material concentrated in the interlaminar regions (due to poor tow impregnation, figure 5) inhibits the proper filling of the resin, thus creating interlaminar voids.

3.4 Binder Effect on Interlaminar Shear Strength

The results of the short beam shear test are displayed in table 3, and figure 13. The results indicate that the incorporation of both binder types into woven glass-reinforced vinyl ester composite laminates results in lower interlaminar shear strengths. The effect becomes more pronounced as additional binder is used in the preform. Although both binders proved to be detrimental in regards to shear strength, the composite laminates with the PRETEX binder fared better. A laminate with 9 weight-percent ATLAC binder resulted in a reduction of interlaminar shear strengths by ~23%, whereas the laminate with 9 weight-percent PRETEX binder resulted in a reduction of ~15%. This reduction in interlaminar shear strengths is most likely due to the increased interlaminar void content resulting from the introduction of the binder as discussed earlier.

Table 3. Interlaminar shear strengths of glass reinforced vinyl ester composite laminates with varying binder concentrations.

Binder Loading	Interlaminar Shear Strength, (N/cm ²)	
	ATLAC 363E	PRETEX 110
No binder	4615 ± 204	4615 ± 204
3%	4407 ± 115	4463 ± 182
6%	3967 ± 182	4139 ± 222
9%	3576 ± 173	3921 ± 271

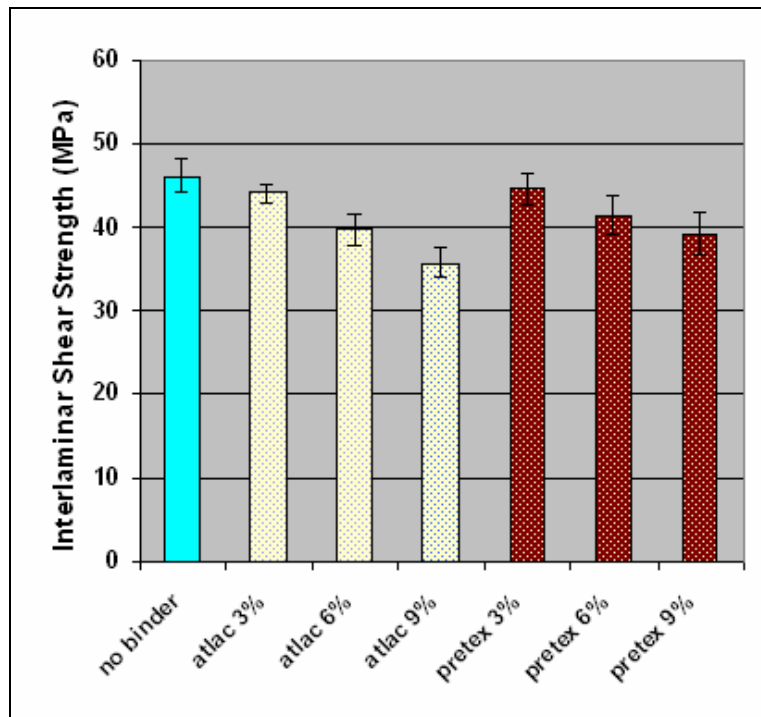


Figure 13. Interlaminar shear strengths of composite laminates manufactured from woven glass preforms of varying binder type and concentration.

3.5 Binder Effect on Interlaminar Fracture Toughness

Figure 14 shows the load-vs.-displacement curve for three individual composite DCB specimens, that of the pure resin and glass fabric without binder, a composite laminate with 9 weight-percent (with respect to glass mat weight only) ATLAC binder and a laminate with 9 weight-percent PRETEX binder. These plots are representative of the other specimens tested in each respective sample set. As the resulting data shows, composites with the PRETEX binder showed higher fracture toughness values compared to the control composite panel (no binder), whereas the composites made from preforms using the ATLAC binder showed lower fracture toughness values. Additionally, from figure 14, it is seen that each specimen exhibited a crack propagation that followed a “stick-slip” type of failure indicated by the jagged peaks in the plot. However, as indicated in figure 14, it was noticed that the composite panels containing the PRETEX binder showed the most stable propagation, with many more smaller crack propagations during loading.

The results of the testing can be seen in figures 15 and 16 and in table 4. Many samples exhibited an R-curve (resistance curve) behavior, although, this type of behavior was not seen with many of the specimens containing ATLAC binder.

From the results, it is seen that the introduction of the ATLAC binder into the composite laminate caused detrimental effects on the Mode I interlaminar fracture toughness. There is nearly a 60% decrease in the G_{IC} propagation, between the composite panel with no binder, and that with a 9 weight-percent loading of the ATLAC binder. On the other hand, it is seen that the introduction of the PRETEX binder has the opposite effect, and the interlaminar fracture toughness G_{IC} propagation, is increased by ~50% at binder loadings of 6 and 9 weight-percent.

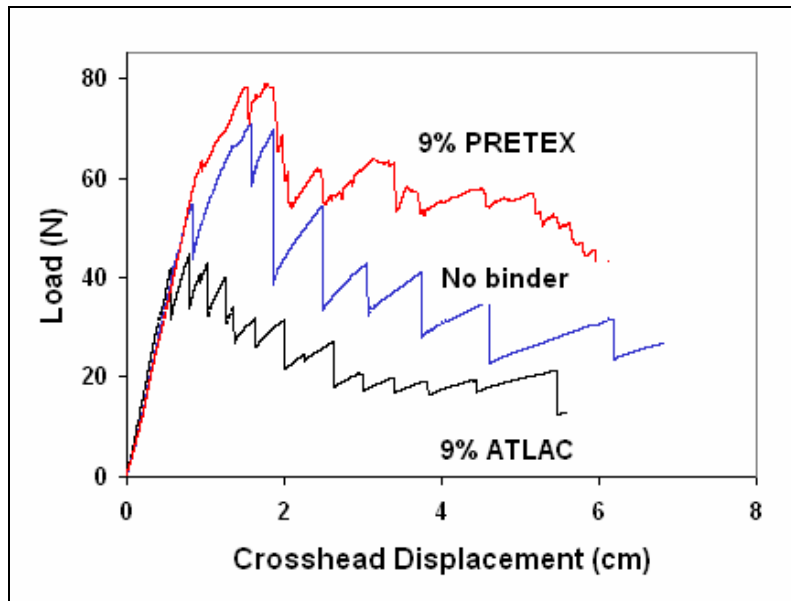


Figure 14. Load vs. displacement of composite DCB specimens.

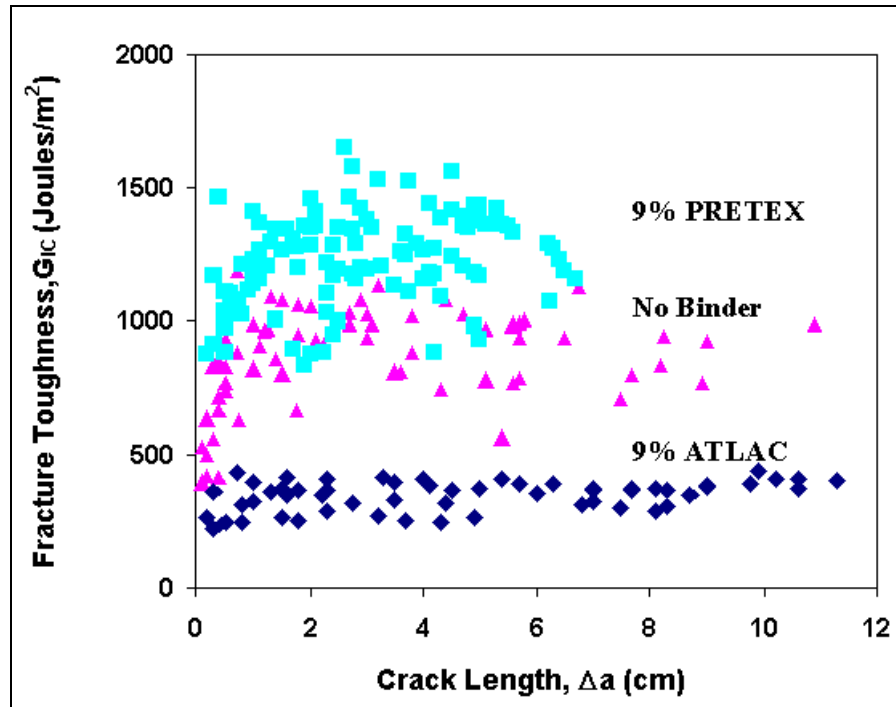


Figure 15. Delamination curve showing R-curve behavior for glass-reinforced DERA KANE 411-C-50 vinyl ester composites with varying binder.

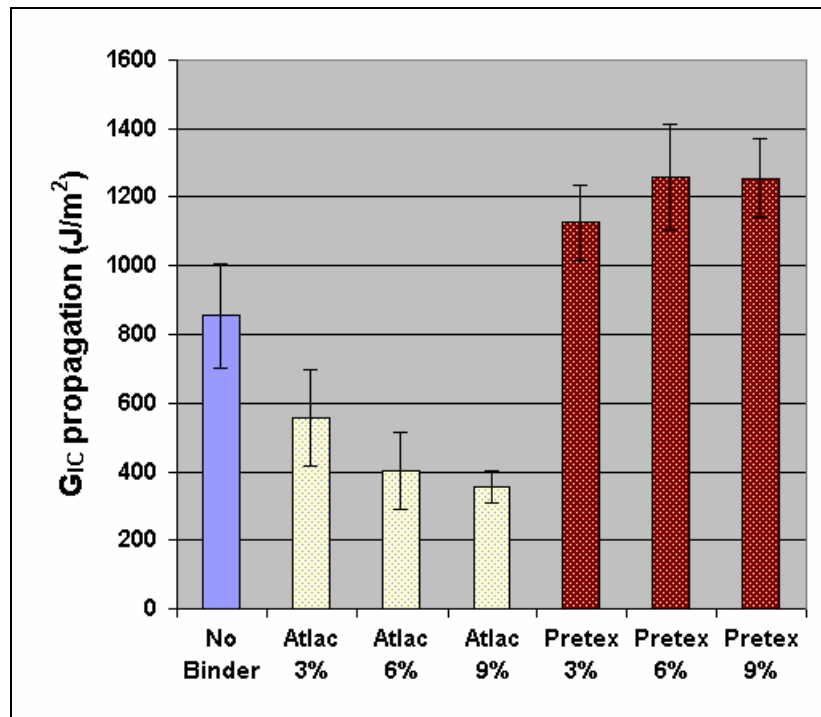


Figure 16. Mode I propagation fracture toughness of composite laminates with varying binder type and concentration.

Table 4. Mode I initiation fracture toughness of composite laminates, G_{IC} , with varying binder type and concentration.

Binder Concentration (Weight-Percent of Fibers)	Interlaminar Fracture Toughness (J/m ²)			
	Laminates With ATLAC		Laminates With PRETEX	
	Initiation G_{IC}	Propagation G_{IC}	Initiation G_{IC}	Propagation G_{IC}
No binder	576 ± 142	855 ± 152	576 ± 142	855 ± 152
3	455 ± 96	560 ± 140	928 ± 105	1126 ± 110
6	291 ± 75	404 ± 112	1096 ± 154	1261 ± 177
9	273 ± 60	357 ± 60	1033 ± 114	1257 ± 169

The improved toughness of the composite laminates containing PRETEX binder is believed to be a result of the high interply adhesion developed during the preforming stages when the binder was cross linked and possibly chemically bound to the fiber sizing. For the case of preforms made with the thermoplastic polyester ATLAC binder, the interply adhesion is solely due to a mechanical interlocking. Thus, there was a much lower interply adhesion with preforms fabricated with this binder. Additionally, if the binder had not completely dissolved, it may act as a barrier between the matrix resin and fiber mat surface, inhibiting proper formation and chemical bonding at the fiber matrix interphase, and result in lower interply toughness.

Subsequent to fracture toughness testing, an SEM was used to examine the fracture surfaces of the specimens. Figure 17 shows the fracture surface of the composite DSB specimen with 9 weight-percent ATLAC loading. It can be seen that much of the failure was of a brittle cohesive type, with smooth and flat fracture surface through the bulk of the matrix. Additionally, it is seen that there exists a cohesive type failure between the fiber and matrix (or binder) interface as indicated by the fiber imprints in the resin.

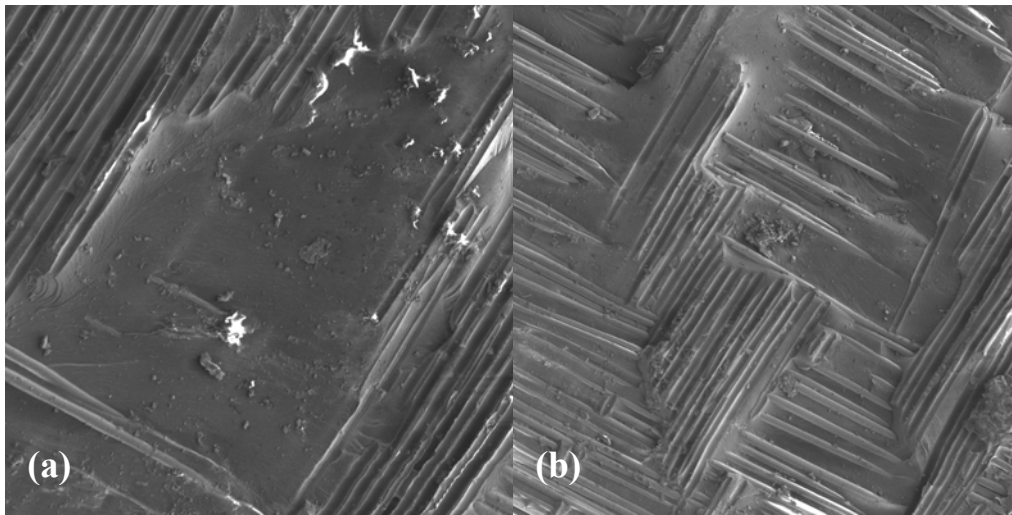


Figure 17. SEM micrographs of fracture surface of DCB specimen of composite laminate containing 9 weight-percent ATLAC (a) 150× (b) 100×.

In the composite specimens consisting of PRETEX binder, the majority of the failure was cohesive between the individual fibers and the matrix (resin or binder) as shown in figure 18. In areas where the failure was through the matrix, the surface consisted of rough pocket-like dimples as shown in figure 18b. In contrast to the ATLAC specimens, this suggests a tougher ductile-type fracture.

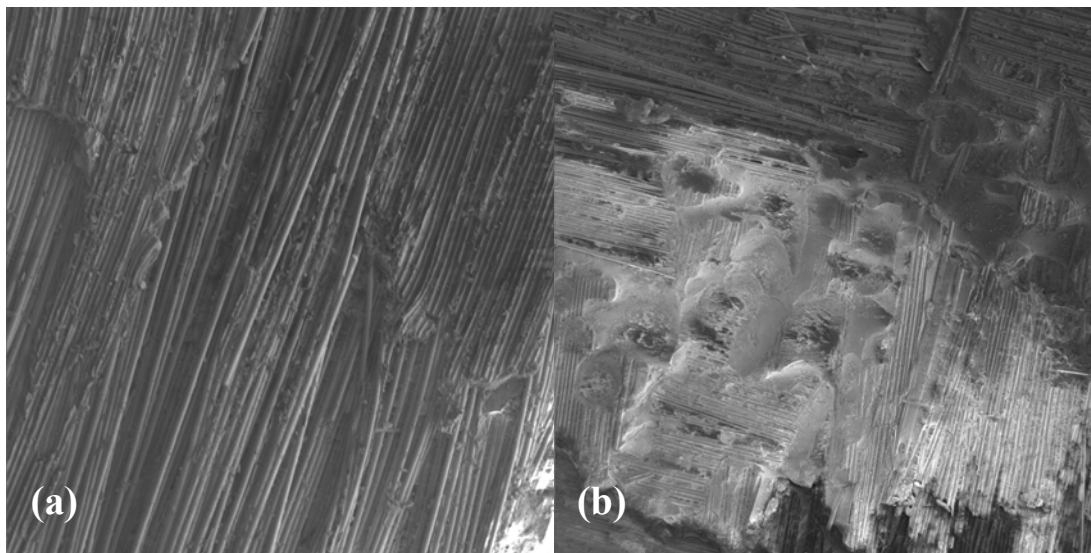


Figure 18. SEM micrographs of fracture surface of DCB specimen of composite laminate containing 9 weight-percent PRETEX at (a) 75 \times and (b) 50 \times .

4. Conclusion

It is concluded that both the ATLAC 363E and PRETEX 110 binders can provide sufficient adhesion between adjacent plies of woven glass mat to construct preforms that are able to maintain their flat shape during handling. With the aid of SEM, it was determined that both binders exhibited similar fiber mat coverage and spread out at their individual processing parameters. SEM images also indicate that both binder materials appear to remain on the surface of the glass fabric, with little or no penetration into the fiber tows.

Results from the T-Peel test show that there is a much greater interply adhesion (15 \times greater at 9 weight-percent binder loading) for preforms constructed with the reactive epoxy (PRETEX) binder than for those with a low-melting thermoplastic (ATLAC). It is believed that the thermoplastic binder simply provides a mechanical interlock between adjacent plies, whereas, if processed correctly, the reactive epoxy binder can provide an additional chemical adhesion with the fiber sizing. This in turn, will result in much better interply adhesion, resulting in a more board-like preform with greater structural integrity. It can be concluded that reactive binders,

which chemically interact with the fiber sizing, are better suited in applications where complex-shaped preforms with little springback are required.

From the SEM analysis of the manufactured composite laminates, it was concluded that the introduction of binder material had led to higher void contents which were concentrated in the interlaminar regions of the composite. Additionally, short beam shear testing concluded that the binder had detrimental effects on the composites interlaminar shear strength. It was determined that this effect became more pronounced at higher preform binder loadings. A composite laminate fabricated from a woven glass preform containing 9 weight-percent ATLAC 363E binder exhibited a reduction of interlaminar shear strength by ~23 weight-percent when compared to that of the same laminate without binder. Likewise, laminates with the 9 weight-percent PRETEX binder exhibited approximately a 15% reduction in interlaminar shear strength. This reduction in interlaminar shear strength is believed to be a result of the increase in interlaminar voids resulting from the binder.

From the Mode I interlaminar fracture toughness testing, it was found that although composites of ATLAC bound preforms showed a decrease in fracture toughness, for composites of PRETEX bound preforms there were substantial improvements. The composite laminate with 9 weight-percent ATLAC binder resulted in a reduction in Mode I propagation interlaminar fracture toughness by ~60%. However, the composites specimens tested with 9 weight-percent PRETEX binder resulted in an increase in fracture toughness by an impressive 47%. Additionally, it was found that the PRETEX specimens exhibited a much more stable fracture, whereas the ATLAC specimens exhibited a “stick-slip” type crack propagation.

From the results, it was realized that one could get a significantly large variation in interlaminar strengths and toughness values by simply varying the binder type and concentration. Thus, this demonstrates the potential for using preform binders to tailor the interlaminar regions of a composite laminate in addition to the inherent benefits provided by the preforms themselves.

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